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Trends in the electronic and geometric structure of non-fullerene based acceptors for organic solar cells

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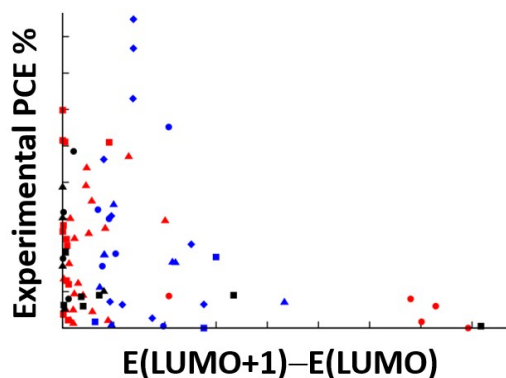
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Broader Context

In just 5 years the maximum efficiency of organic solar cells containing non-fullerene electron acceptors has increased from ~3% to ~12% thanks to the substantial progress in both materials and device optimization. There are now close to a hundreds of non-fullerene acceptors used in high efficiency solar cells, based on a number of different chemical designs. It seems appropriate at this point in time to analyse these compounds in search of some unifying chemical principle and to combine such an exploration with the physical ideas that have guided the design so far. We have found that all high efficiency acceptors are characterized by unusually small energy difference between the two lowest unoccupied orbitals.

Abstract

We constructed a database of 80 high performing non-fullerene electron acceptors and studied the common electronic and geometric properties in search of unifying design rules. We discovered that, without exception, all high performing materials are characterized by very low gap between LUMO and LUMO+1 orbitals, a feature that is consistent with microscopic models and seems to be true for all classes of compounds considered. We also confirmed that non-planarity of the acceptor is beneficial but not for all classes of acceptors. We suggested that by building similar databases and keeping it up to date it will be possible to identify statistically meaningful structure-property relations.



TOC Entry: High power conversion efficiency are displayed by organic solar cells with small energy gap between LUMO+1 and LUMO orbitals

Fullerene electron acceptors have been present in all efficiency record breaking organic solar cells since their initial development.¹ It was recognized by many that having electron acceptors with different chemistry could bring many benefits in terms of light harvesting efficiency, manufacturing cost and, ultimately, commercial viability of the technology.²⁻⁶ A review of the field in 2011⁷ reported only 4 non-fullerene acceptors used in cells with power conversion efficiency (PCE) between 3% and 4% and none with PCE above 4. Today there are close to one hundred different acceptors with efficiency between 3% and 12% and the field is one of the most active in the area of organic solar cells because of the very promising rate of progress.

A number of more recent reviews attempt a classification of the chemistry of the main acceptors^{2, 3} and explain the pace of improvement in terms of our greater understanding of the process of cell optimization including optical modelling, use of additives to improve the morphology and energy level matching with an always increasing library of electron donors. However, it is also clear that the best performing acceptors belong to different chemical class and the strategies pursued to improve them are different. For example a promising family of acceptors based on the perylene diimide (PDI) dye was built on the observation that the isolated PDI molecule forms too large aggregates, a process that can be avoided by substitution with branched side chains or synthesis of non-planar dimers or oligomers.⁸⁻¹⁰ A rather different group of acceptors is based on linear oligomers, synthesized with techniques developed in the area of polymeric semiconductors and often using similar building blocks as benzothiadiazole (BTD),¹¹ diketopyrrolopyrrole (DPP)¹², indacenodithiophene (IDT)¹³ or indacenodithienothiophene (IC).¹⁴ For other type of acceptors (subphthalocyanine (SubPc),¹⁵ tetraazabenzodifluoranthene diimide (BFI)¹⁶) there are for the moment fewer instances, but equally very promising.

Given the large number of high efficiency (molecular) acceptors now known and the substantial chemical difference among them, it is possibly appropriate at this point in time to analyse the electronic structure properties of the high performing acceptors in search of some common features. The analysis of large databases in search of structure-property relations is very common in the pharmaceutical sciences¹⁷ and is gradually emerging as a useful tool also in the area of organic and hybrid electronics.¹⁸⁻²⁰ In a recent survey of organic dyes used in dye sensitized solar cells it emerged that, contrary to expectation, the donor-pi-acceptor character of the dye is not correlated with the solar cell efficiency.²¹ On the other hand, the expected correlation was found with the reorganization energy and the oxidation free energy.²²

In this work we will build an unbiased large set of electron acceptors reported in literature and, after evaluating their electronic structure and geometry with computational methods, we test few hypotheses on the relation between electronic structure and efficiency in a solar cell. The database is made available in the supporting information to test further hypotheses and/or update it with new compounds.

The selection of the compounds to be included in such a database should be based on a systematic and reproducible procedure to avoid any possible bias. However, one should recognize that very poorly performing solar cells are not reported in literature and those that are deemed to be not very promising are not fully optimized. We therefore construct a database trying to capture as many acceptors as possible displaying (average) PCE above 3%. We proceeded as follows:

- (a) We performed various searches using the Web of Science Database in the 2010-2016 time window, using keywords such as "high-efficiency semiconductor", "efficient nonfullerene acceptor", and related keywords. The searches returned a total of 379 articles, of which 26 reporting acceptors with PCE \geq 3%.
- (b) 15 of the 26 articles selected above reported PCE \geq 5%. All papers citing these 15 articles have been included in the database, bringing the total number of article evaluated to 456.

- (c) In the total database of 456 articles, we identified 39 papers reporting acceptors with PCE \geq 3%, for a total of 80 distinct acceptors. In case of review papers reporting the maximum PCE, we checked the original paper cited and used the average PCE value from that source.

Table 1 reports the list of considered acceptors in the form of a literature reference and the label used in the original paper. We have used the average PCE when average and maximum were given, and the largest average if a compound was used in different studies or with different devices. The donor used in the best performing cell is also reported. In the table we have also introduced a rough classification of the acceptors to help the discussion of the results. We have considered the group of acceptors containing PDI and, within this group, noted if PDI appears as monomer (PDI(1)), dimer PDI(2), trimer or larger (PDI(3+)). We have then considered the molecules formed by linearly coupled oligomers in a pattern ABA and labelled them as L(IDT), L(BDT), L(DPP) or L(oth) if they contained the IDT, BDT, DPP or none of these fragments respectively (the acceptors with highest PCE belong to this class and contain indacenodithienothiophene monomer). We have also labelled the subphthalocyanines (SubPc) and the acceptors containing the DBFI fragment.

Standard density functional theory optimization in the gas phase has been performed for all acceptors at the 6-31G*/B3LYP level and the electronic and geometric properties have been evaluated on the optimized geometries.²³ To make the calculation feasible and since the focus is on the conjugated core of the molecules rather than the side chains added to improve the solubility, we removed long alkyl chains according to the following criteria: (i) linear alkyl chains with more than two carbons or branched chains where the branching is not on the first carbon atom are replaced by an ethyl group; (ii) side chains with branching on the first carbon atom are replaced by an isopropyl group; (iii) alkoxy side chains are replaced by the methoxy group; (iv) side chains containing the ether group are treated as other alkyl chains.

All acceptors in the database have been used in conjunction with suitable donor materials in organic solar cells, i.e. a good alignment is a prerequisite for all good acceptors but clearly not what makes a material particularly good. A critical property is the ability of the acceptor to form phase separated morphologies with the donor, ideally of the same characteristic size of the exciton diffusion length. This property is clearly not easy to derive from the geometric and electronic structure of the isolated acceptor and it is also fairly difficult to design from chemical intuition (besides the usual means proposed to modify the solubility in different solvent by changing the side groups). However, many authors have proposed that non-planarity of the molecule is beneficial because it promotes amorphous phases, prevents strong aggregation and facilitates charge transport in three dimensions.²⁴ Such property can be easily monitored across the database and it is relatively easy to incorporate in the design of new molecular electron acceptors. Another proposal is that the ideal acceptor has a low lying LUMO+1 level, which accelerates the charge separation at the interface (see energy level diagram in Figure 1). This proposal, originally based on a very simple dimer model,²⁵ was generalized for more realistic interfaces and more advanced physical models.^{26, 27} Also this property is simple to assess from the electronic properties of the isolated donor and it can be easily built in the acceptor by design. It can be noted that fullerene derivatives, non-planar and with quasi degenerate low-lying virtual orbitals, satisfy both criteria - as it should be.

In the Table and the related Figure 2, we report the energy difference between LUMO+1 and LUMO orbitals computed for the neutral molecule. As a measure of the planarity of the conjugated core we report the root mean square distance of the sp^2 carbon atoms from the best plane passing across them, $RMSD_p$. For a planar molecule the plane is the one perpendicular to the principal axis of inertia with the largest angular moment of inertia. The same plane defines the "best" fitting plane across a number of points, i.e. that one minimizing the sum of the squared distance between the plane and all points. Alternative measures of non-planarity do not change the results and are not reported.

Figure 2a illustrates the correlation between the energy difference between LUMO+1 and LUMO (referred to as $\Delta LUMO$) and the PCE reported for the selected electron acceptors. The main striking feature is that all the 22 acceptors with PCE larger than 6% have $\Delta LUMO$ smaller than 0.5 eV and for 21 of them $\Delta LUMO$ is smaller than 0.3 eV. First of all, one should note that this is not typical of molecular semiconductors, for example all the 5 acceptors considered in a similar analysis²⁵ (and based on pre-2012 papers) have all $\Delta LUMO$ larger than 0.9 eV. A second important point is that all the efficient molecular semiconductors belong to different chemical classes and they have low $\Delta LUMO$ for different reasons. Some of them are weakly interacting dimers or trimers of PDI and they are obviously expected to have low $\Delta LUMO$ as suggested for example in ref. ²⁵. Many of them are more difficult to consider as weakly interacting dimers but, being formed by an ABA sequence of monomers, they may have some built-in tendency to have LUMO and LUMO+1 of similar energies. For others (e.g. the DBFI molecule) the small $\Delta LUMO$ could not be easily predicted without an electronic structure calculation. Overall the data seems to suggest that a low $\Delta LUMO$ is a necessary condition for high performing electron acceptors (while clearly not a sufficient one). One may also argue, but the data are possibly not dense enough, that a small $\Delta LUMO$ in the 0.2-0.3 eV range is preferable to a vanishing $\Delta LUMO$.

The analysis of the non-planarity gives less clear-cut indications. From the data in Figure 2b it seems that both planar and non-planar molecules are equally likely to give high performing materials, or, more precisely, about half of the molecules with PCE larger than 5% show a deviation from planarity of more than 1 Å. The data may suggest that there is no special electronic advantage in having non-planar molecules but a degree of non-planarity could have a beneficial effect on the morphology of the blend. Such property is however a solid state property of the mixture rather than a true molecular property.

There is a well-known risk that one can find misleading correlations between physical quantities, which are not particularly helpful in informing the synthesis and the physical understanding. A small $\Delta LUMO$, proposed here to be necessary condition for high performance electron acceptors, could be in principle associated simply with larger molecules, which in turn could be better because of greater delocalization and smaller reorganization energy. In Figure 3 we show that there is no correlation in the data set between size of the molecule and PCE, i.e. it is not the molecular size but the actual position of the LUMO+1 energy level that makes an acceptor potentially better.

It is to some extent surprising that correlations could be found between an isolated acceptor property and device efficiency, while it is very well established that the morphology of the blend and the correct alignment of the donor and acceptor energy levels are expected to be more important.²⁸⁻³¹ It should be stressed that these remain the most critical parameters for the efficiency of the cell if one considers a random sample of devices. In order for a property of the isolated electron acceptor to emerge so clearly from the data set one must assume that the efficiency for each acceptor has been at least partially optimized with respect to the rest of the parameter space. In practice, all the reported data points correspond to the best average efficiency of a single acceptor after testing it with a number of alternative donors and experimental conditions. In many cases the other donors are reported in the published works, but it is to be expected that very poor devices (because of poor energy alignment or poor morphology) were not reported. The only reason for being able to focus on an acceptor-only property is because we have selected data points that have been (to some extent) optimized for other relevant properties.

Similarly, the key elementary processes in organic solar cells (charge generation at the interface, charge diffusion away from the interface, geminate and non-geminate recombination) are properties of the donor-acceptor interface, not the acceptor alone. Recent works highlight the difficulty in modelling the interface geometrical and electronic structure,³²⁻³⁵ its electrostatics³⁶ and the quantum dynamics of the elementary processes.³⁷⁻⁴¹ A large collection of electronic structure calculations like the one presented here cannot replace a detailed physical modelling of the interfacial processes but

can nevertheless provide useful insights. For example, our data suggest that the modelling of charge generation at the interface with fullerene derivatives or these high efficiency acceptors should include a number of virtual orbitals per molecule, and not just the LUMO.

This work demonstrates once more that a productive approach in material science development is to combine bottom-up approaches, where physical principles are used to suggest mechanisms and design, and top-down approaches, where a large set of experimental data set is used to test hypotheses on structure property relations. We have now a strong indication from the combination of both approaches that high efficiency electron acceptors should have low energy LUMO+1 orbitals, a property easy to build in new efficient acceptors or to test on hypothetical compounds before they are synthesised.

Supporting Information. The Cartesian coordinates of all acceptors considered are provided in a format suitable for alternative analyses.

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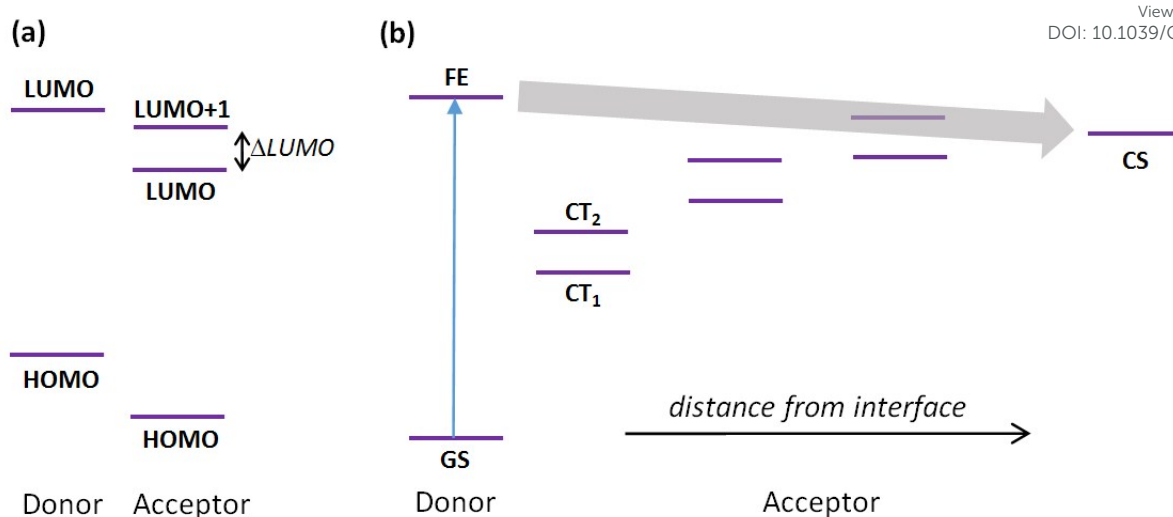


Figure 1. (a) One-electron energy levels of isolated electron donor and acceptor. If LUMO+1 of the acceptor is sufficiently low it can accept an electron from the LUMO of the donor. (b) Electronic state energy level diagram showing the ground state (GS), the Frenkel exciton localised on the donor (FE) and the charge transfer states (CT_i) of increasingly high energy at higher distance from the interface. According to ref. 25-27 the efficient formation of charge separated (CS) state (grey arrow) can be helped by the presence of higher energy CT states, promoted by low $\Delta LUMO$ gap.

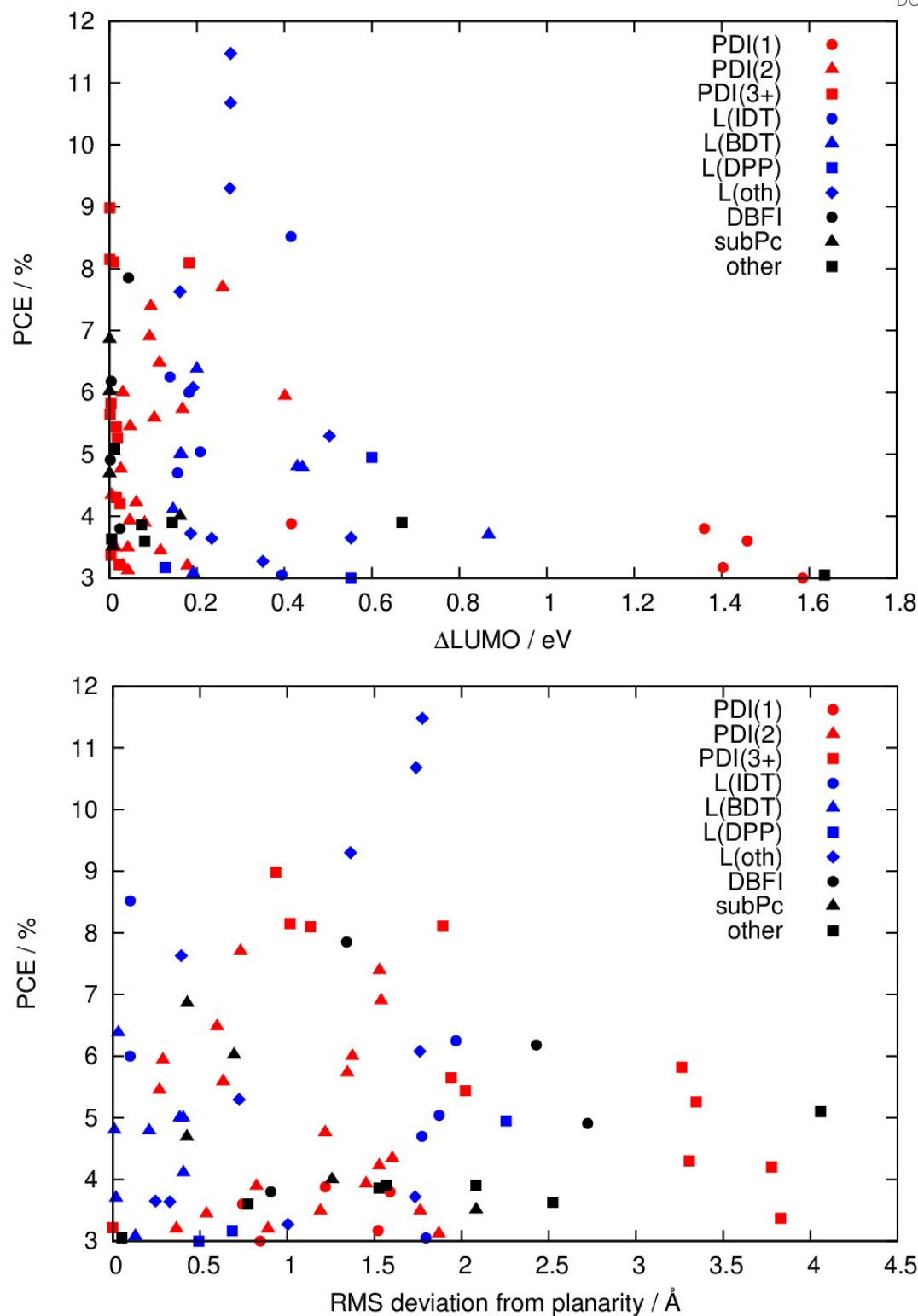


Figure 2. (top) Computed difference between LUMO+1 and LUMO energy versus experimental PCE for a device containing a given electron acceptor. The acceptors are classified as described in the text. (bottom) Computed deviation from the molecular plane versus experimental PCE.

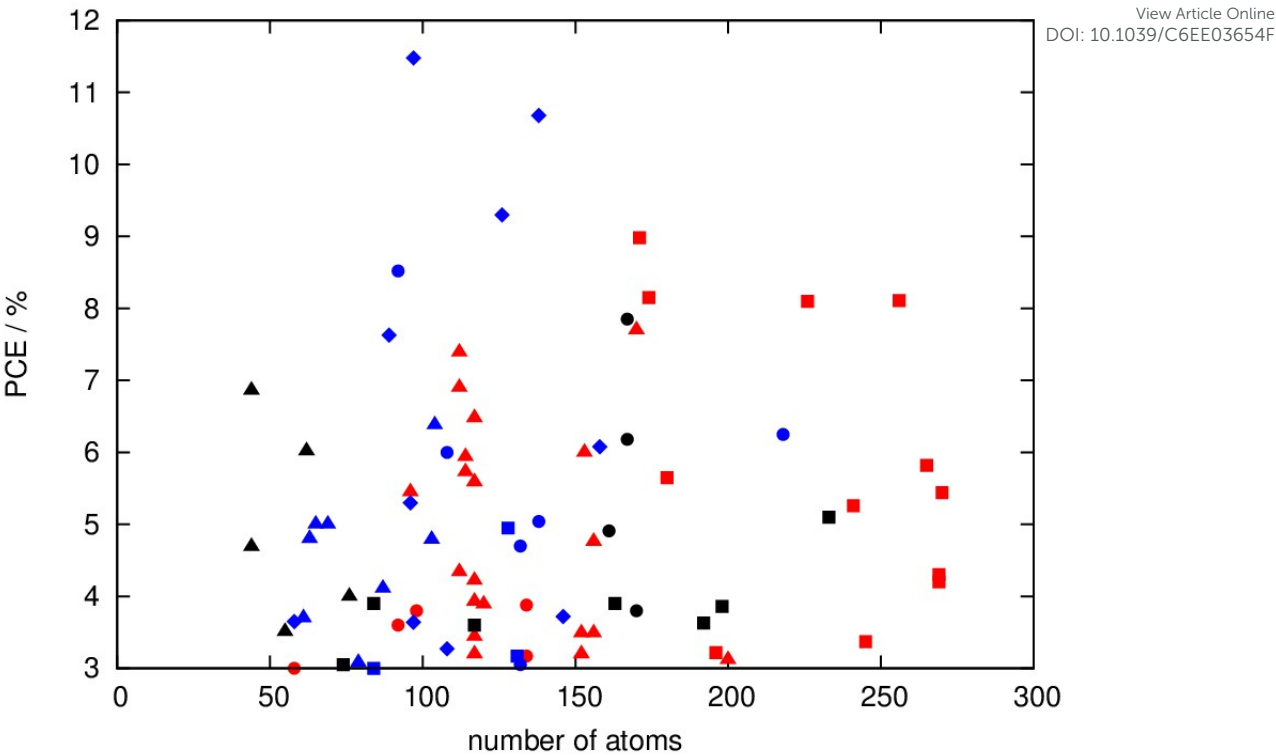


Figure 3. (Lack of) correlation between molecular size and measured PCE for the considered data set. The point symbols/colours have the same meaning than Figure 1.

Table 1. List of acceptors and associated properties. The acceptor is identified by the label used for it in the reference given in the first column. If a larger PCE was later reported an additional reference is given after the PCE value in the last column. The donor is the one used for the reported PCE. The chemical classification in the 4th column is explained in the main text. The number of atoms refer to the acceptor after reduction of side-chain length. $RMSD_p$ defined in the text.

Ref.	Acceptor's Label	Donor's Label	Chem. Class	No of Atoms	LUMO (eV)	LUMO+1 (eV)	$\Delta LUMO$ (eV)	$RMSD_p$ (Å)	PCE (%)
³	c1	<i>p</i> -DTS(FBTTh ₂) ₂	PDI(1)	58	-3.4208	-1.8357	1.5851	0.8440	3.00
³	c11	PBDTTT-C-T	PDI(3+)	196	-3.2627	-3.2410	0.0218	0.0000	3.22
³	c5	PBDTTT-C-T	PDI(2)	117	-3.3664	-3.3052	0.0612	1.5270	4.22 ⁴²
⁴³	DTDFBT(TDPP) ₂	PTB7	L(BDT)	103	-3.0344	-2.5930	0.4414	0.2080	4.79
⁴⁴	DBFI-MTT	PSEHTT	DBFI	170	-3.3150	-3.2913	0.0237	0.9050	3.80
²	1.11a	PSEHTT	DBFI	161	-3.3231	-3.3209	0.0022	2.7230	4.91 ⁴⁵
²	1.11b	PSEHTT	DBFI	167	-3.3054	-3.3014	0.0041	2.4280	6.18 ⁴⁴
²	1.1b	PBDT-TS1	PDI(2)	96	-3.3988	-3.3517	0.0471	0.2660	5.45
²	1.2	PBDTT-F-TT	PDI(2)	114	-3.5988	-3.4320	0.1668	1.3440	5.73 ⁴⁶
²	1.3	PDBT-T1	PDI(2)	112	-3.5503	-3.4587	0.0917	1.5380	6.90
²	1.4	PBDTT-F-TT	PDI(2)	114	-3.5650	-3.1639	0.4011	0.2860	5.94 ⁴⁷
²	1.6	PBDTT-F-TT	PDI(3+)	270	-3.4244	-3.4086	0.0158	2.0210	5.44
²	1.7a	PffBT4T-2DT	PDI(3+)	269	-3.4211	-3.4053	0.0158	3.3060	4.30
²	1.7b	PffBT4T-2DT	PDI(3+)	269	-3.4502	-3.4265	0.0237	3.7780	4.20
²	1.8	PffBT4T-2DT	PDI(2)	153	-3.3770	-3.3463	0.0307	1.3730	6.00 ⁴⁸
²	1.9	PBTI3T	PDI(1)	92	-3.2935	-1.8349	1.4586	0.7440	3.60 ⁴⁹
²	2.10b	PTB7	subPc	55	-3.1068	-3.0997	0.0071	2.0830	3.5 ⁵⁰
²	2.5	P3HT	other	74	-2.5223	-0.8874	1.6349	0.0500	3.05
²	2.6	6T	subPc	44	-2.5819	-2.5816	0.0003	0.4240	4.69
²	2.7	6T	subPc	62	-2.4997	-2.4994	0.0003	0.6950	6.02
²	2.8	2.7	subPc	44	-3.2567	-3.2562	0.0005	0.4260	6.86
²	2.9	2.6	subPc	76	-3.6646	-3.5030	0.1616	1.2560	4.00
²	3.1	P3HT	L(BDT)	87	-3.2268	-3.0812	0.1456	0.4040	4.11
²	3.2a	PBDTTT-C-T	L(oth)	146	-3.2984	-3.1125	0.1859	1.7330	3.72 ⁵¹
²	3.2b	PTB7-TH	L(oth)	158	-3.2388	-3.0477	0.1910	1.7610	6.08 ⁵²
²	3.3	P3HT	L(BDT)	79	-2.8613	-2.6698	0.1916	0.1280	3.08

2	3.4	PBDB-T	L(oth)	138	-3.3449	-3.0676	0.2773	1.7390	10.68 ⁵³
2	3.5	P3HT	L(DPP)	131	-2.5892	-2.4619	0.1274	0.6840	3.17
2	3.6	<i>p</i> -DTS(FBTTh ₂) ₂	L(oth)	96	-3.1460	-2.6428	0.5031	0.7240	5.30
2	3.7a	P3HT	L(BDT)	104	-3.3120	-3.1120	0.2000	0.0310	6.38
54	TPB	PTB7-Th	PDI(3+)	256	-3.5041	-3.4943	0.0098	1.8920	8.11
55	f7	Molecule T	PDI(1)	134	-3.1016	-1.6986	1.4030	1.5210	3.17
55	f8	Se-SM	PDI(1)	134	-3.6192	-3.2034	0.4158	1.2190	3.88
56	2c	PTB7-Th	PDI(2)	112	-3.4195	-3.4146	0.0049	1.6020	4.34
12	DPP5	P(PTQD-BDT)	other	84	-3.4448	-2.7762	0.6686	1.5660	3.90
12	DPP6	P(PTQD-BDT)	L(DPP)	128	-3.8802	-3.2799	0.6003	2.2550	4.95
8	alphaPBDT	PBT7-Th	PDI(2)	156	-3.4295	-3.4040	0.0256	1.2170	4.76
8	alphaPPID	PBT7-Th	PDI(2)	152	-3.4829	-3.4693	0.0136	1.1900	3.49
8	betaPBDT	PBT7-Th	PDI(2)	156	-3.4320	-3.3901	0.0419	1.7630	3.49
8	betaPPID	PBT7-Th	PDI(2)	152	-3.4742	-3.4434	0.0307	0.8900	3.20
57	SdIPBI-Se	PDBT-T1	PDI(2)	112	-3.5237	-3.4290	0.0947	1.5290	7.39
10	SF-PDI4	PV4T2FBT	PDI(3+)	265	-3.4241	-3.4203	0.0038	3.2630	5.82
9	SBF-PDI4	PTB7-Th	PDI(3+)	241	-3.4693	-3.4513	0.0180	3.3450	5.26
58	NI-AA-NI	P2	L(oth)	58	-3.1479	-2.5957	0.5521	0.2440	3.65
59	DPP-PHt2	P3HT	L(DPP)	84	-3.0739	-2.5217	0.5521	0.4930	3.00
60	TP-PDI	PTB7-Th	PDI(1)	98	-3.2505	-1.8901	1.3603	1.5900	3.80
4	M10	P3HT	other	163	-2.8676	-2.7242	0.1434	2.0820	3.90 ²⁴
4	M18	P3HT	L(BDT)	61	-3.1318	-2.2646	0.8672	0.0180	3.70
4	M32	DBP	other	117	-3.0627	-2.9822	0.0805	0.7750	3.60
4	PDI6d	PBDTTT-C-T	PDI(2)	117	-3.3520	-3.3057	0.0463	1.4520	3.93 ⁶¹
4	PDI9	BDT-T-DPP	PDI(2)	200	-3.2752	-3.2331	0.0422	1.8690	3.12 ⁶²
14	ITIC-Th	PTBT-T1	L(oth)	126	-3.3454	-3.0698	0.2757	1.3620	9.30
63	CBM	PCE10	L(BDT)	65	-3.6478	-3.4834	0.1644	0.3830	5.00
63	CDTBM	PCE10	L(BDT)	63	-3.8968	-3.4674	0.4294	0.0080	4.80
63	FBM	PCE10	L(BDT)	69	-3.6597	-3.4976	0.1622	0.4030	5.00
13	IDT-IC	PTB7-Th	L(IDT)	132	-3.4001	-3.0061	0.3940	1.7960	3.05
13	IDTIDT-IC	PTB7-Th	L(IDT)	218	-3.1302	-2.9920	0.1382	1.9670	6.25
64	NIDCSN	<i>p</i> -DTS(FBTTh ₂) ₂	L(oth)	108	-3.0393	-2.6886	0.3508	1.0030	3.27
5	IC-C6IDT-IC	PDBT-T1	L(IDT)	92	-3.4978	-3.0829	0.4150	0.0990	8.52

5	M10	P3HT	other	192	-2.6442	-2.6393	0.0049	2.5230	3.63
65	DTBTF	DR3TSBDT	L(oth)	97	-3.0758	-2.8423	0.2335	0.3260	3.64
66	IDTT-2BM	PBDTTT-C-T	L(IDT)	132	-3.6102	-3.4546	0.1557	1.7720	4.70
6	FPDI-F	PTB7-Th	PDI(2)	117	-3.4314	-3.2535	0.1780	0.3640	3.20 ⁶⁷
6	FPDI-Se	PTB7-Th	PDI(2)	117	-3.3890	-3.2864	0.1026	0.6320	5.59 ⁶⁷
6	FPDI-T	PTB7-Th	PDI(2)	117	-3.4056	-3.2913	0.1143	0.5960	6.48 ⁶⁷
6	hPDI3	PTB7-Th	PDI(2)	170	-3.6336	-3.3748	0.2588	0.7310	7.70 ⁶⁸
6	hPDI4	PTB7-Th	PDI(3+)	226	-3.6723	-3.4899	0.1823	1.1320	8.10 ⁶⁸
6	tetra-PDI	PTB7-Th	PDI(3+)	245	-3.4692	-3.4660	0.0032	3.8290	3.37 ⁶⁹
70	BPDI3	PTB7-Th	PDI(3+)	180	-3.5234	-3.5223	0.0011	1.9410	5.65
71	SFDPPB4	P3HT	other	233	-2.6075	-2.5957	0.0117	4.0590	5.10
72	EH-IDTBR	P3HT	L(IDT)	108	-2.9536	-2.7718	0.1818	0.0980	6.00
73	DICTF	PTB7-Th	L(oth)	89	-3.3248	-3.1637	0.1611	0.3920	7.63
74	4D	P3HT	other	198	-2.6581	-2.5849	0.0732	1.5260	3.86
75	Ph2a	PBDTT-FTTE	PDI(2)	120	-3.3746	-3.2943	0.0803	0.8230	3.89
75	T2	PBDTT-FTTE	PDI(2)	117	-3.4026	-3.2861	0.1165	0.5370	3.44
76	4a	PDBT-T1	PDI(3+)	174	-3.4344	-3.4336	0.0008	1.0160	8.15
76	6a	PDBT-T1	PDI(3+)	171	-3.4358	-3.4350	0.0008	0.9350	8.98
16	DBFI-EDOT	PSEHTT	DBFI	167	-3.3101	-3.2668	0.0433	1.3390	7.85
77	IDT-2BR	P3HT	L(IDT)	138	-3.3248	-3.1174	0.2074	1.8710	5.04
78	IT-M	PBDB-T	L(oth)	144	-3.3079	-3.0309	0.2770	1.7755	11.48

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